



Semi-interpenetrating polymer networks as solid polymer electrolytes: Effects of ion-dissociation, crosslink density and oligomeric entanglements on the conductivity behavior in poly(ethylene oxide)–polyurethane/poly(acrylonitrile) matrix

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HIGHLIGHTS

- Aspects of structural modifications on a promising semi-IPN electrolyte are reported.
- Dependence of ion-dissociation and matrix conductivity on the nature of salt used.
- Network crosslink density depends on PEG chain length and affects ion conductivity.
- Use of an entangled oligomer to effectively plasticize and create a ternary system.
- Results demonstrate versatility of these semi-IPNs to be custom designed as SPEs.

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ABSTRACT

The present study investigates into three aspects of tailoring and simple structural modifications on a promising solid polymer electrolyte system of poly(ethylene oxide)–polyurethane/poly(acrylonitrile) semi-interpenetrating polymer networks. Influence of the nature of salt solvated, cation/anion mobility, ion–polymer interaction and transient crosslink formation is evaluated using different solvated electrolytes and the conductivity achieved varied as $\text{LiClO}_4 \geq \text{LiCF}_3\text{SO}_3 > \text{NaBF}_4 > \text{NaClO}_4 > \text{KI}$. The role of optimum chain length between the crosslinks (crosslink density) necessary to attain better conductivity levels is appraised using PEG of different molecular weights (400, 2000, 4000, 10,000 and 35,000) for synthesis and the maximum conductivity was obtained for PEG-4000. The temperature dependence of ion conductivity shows an Arrhenius to VTF transition at ~ 323 K in these semi-IPNs, a general behavior independent of the nature of salt and the poly(ethylene glycol) chain length. Ternary composition of semi-IPN containing 30 wt% PEGDME MW 500 yields a conductivity of $\sim 2 \times 10^{-5} \text{ S cm}^{-1}$ at 35°C , an order of magnitude higher than that obtained without plasticizing component. VTF behavior is witnessed throughout the temperature window in the study for samples with oligomeric plasticization. Linear sweep voltammetry indicates significantly good electrochemical stability (~ 4.6 V) of the semi-IPN electrolyte matrix.

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1. Introduction

The goal of achieving an ideal polymer electrolyte (PE) suitable for realizing practical application is still elusive and several gaps and bottlenecks remain to be addressed. Structural modification of

PEO based systems to improve their physical properties and conductivity behavior is still an open challenge in the field of solid polymer electrolytes. Redesigning the polymer architecture to incorporate optimal distribution of solvating groups for cation coordination, minimization of chain regularity to reduce crystallinity and enhancing chain flexibility have been identified as some of the most suitable strategies to develop superior SPEs. In this direction, various classes of polymeric materials such as random copolymers [1–8], block copolymers [9–11], comb polymers [12–14] and crosslinked networks [15–18] have been explored and documented. The nature (cation/anion) and concentration of the

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incorporated salt used can affect the conductivity by influencing the formation of crystalline domains, intermolecular crosslinking and phase composition. Thus, the electrolyte properties can be suitably modified by incorporating different salts into the matrix [11,19]. For network systems, the crosslink density *i.e.* the molecular weight of the polymeric chains between the crosslinks, too plays a significant role in the ion conducting behavior of the electrolyte matrix.

In combination with these simple structural modifications, further plasticization of the polymer matrix is a widely employed approach to improve the overall performance of the polymer electrolytes [20–39]. Plasticizers used in ‘gel’ polymer electrolytes are usually low molar mass organics, preferably having a high dielectric constant to ensure strong charge dissociation and provide a liquid-like environment within the polymer matrix, which facilitates ion transport. Propylene carbonate (PC) [20–23], ethylene carbonate (EC) [38,39], dimethyl carbonate (DMC) [35], diethyl carbonate (DEC), γ -butyrolactone and the likes, are some of the conventional organic liquids commonly used for the purpose. Low molecular weight glycols, such as diglyme, tetraglyme (TGME) and polyethylene glycol dimethylether (PEGDME) have also been exploited [28–33]. Ideally, the system behaves like a liquid with high ionic conductivity, while preserving the dimensional stability of the solids.

The feasibility of using poly(ethylene oxide)–polyurethane/poly(acrylonitrile) (PEO–PU/PAN) semi-interpenetrating polymer networks (semi-IPNs) and its nano-composites as solid polymer electrolytes have been demonstrated by our group in recent years [40–44]. The attempts have resulted in a promising SPE with room temperature ionic conductivity of $\sim 10^{-6} \text{ S cm}^{-1}$, while retaining the necessary dimensional and thermal stability required for a polymer electrolyte. Useful insights into the various aspects of the electrochemical behavior of these systems and their dependence on the physico-chemical properties gained from these studies provided reasonable grounds for tailoring the system further.

In continuation with our efforts to enhance the ionic conductivity whilst creating an effective library of these semi-IPN matrices, the present paper, reports some of the interesting findings pertaining to various simple structural modifications that have generated important leads toward developing an ideal SPE for practical purposes. This endeavor investigates into three aspects of structural modifications on the PEO–PU/PAN semi-IPN system and their impact on the ionic conductivity behavior: *viz.*, i) the nature of salt (ion-dissociation), ii) crosslink density of the PEO–PU network (PEG chain length) and iii) creating a ternary system using an entangled oligomer within the semi-IPN matrix (oligomeric plasticization) have been assessed. The results presented herein, provide a more comprehensive understanding of the complex matrix behavior for the PEO–PU/PAN semi-IPNs and affirm our contention of the potential use of such systems as solid polymer electrolytes.

2. Experimental

2.1. Materials

Castor oil (BSS Grade), diphenylmethane diisocyanate (MDI) (Ind-ital Chem. Ltd.), polyethylene glycol (PEG), (MW = 400, 2000, 4000 from SD Fine Chemicals and MW = 10,000, 35,000 from Fluka), N,N-dimethylaniline (DMA) (SD Fine Chemicals), acrylonitrile (SRL), benzoyl peroxide and tetrahydrofuran (THF) (Ranbaxy), lithium perchlorate (LiClO_4) (Aldrich), lithium trifluoromethanesulfonate (LiCF_3SO_3) (Aldrich), sodium perchlorate (NaClO_4) (Aldrich), sodium tetrafluoroborate (NaBF_4) (Merck), potassium iodide (KI) (SD Fine Chemicals), polyethylene glycol dimethylether (PEGDME, MW = 500) (Aldrich) were used as obtained.

2.2. Synthesis of PEO–PU/PAN (60/40) semi-IPNs

2.2.1. Variation of salt

In a typical reaction, the isocyanate terminated urethane prepolymer is synthesized by reacting castor oil with excess of MDI in THF for 1 h at room temperature under nitrogen atmosphere as reported elsewhere [40–43, see Supporting information]. The desired amount of various salts to be added for each composition is calculated from the EO/M^+ mole ratio ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$). The EO/M^+ mole ratios (salt concentration) used in the present study are 30, 20, 15 and 10 (Table 1). The required amount of salt is mixed with PEG and dissolved in acetonitrile/THF (2:1) prior to its addition to the prepolymer. The PEG containing the desired amount of salt, the second monomer acrylonitrile (40 wt%), benzoyl peroxide (initiator) and N,N-dimethylaniline (catalyst) is then added to the prepolymer. For the synthesis of the poly(ethylene oxide)–polyurethane networks a $-\text{OH}/-\text{NCO}$ ratio of 1:1.25 is maintained. The mixture is again degassed and stirred under nitrogen atmosphere at room temperature for 30 min. The viscous solution is then cast in

Table 1

Electrolyte compositions of PEO–PU/PAN (60/40) semi-IPNs studied with respect to the molecular weight of PEG used, type of salt, weight % of oligomer PEGDME 500, the EO/M^+ mole ratio, the Arrhenius activation energy (ΔE_a) and the Vogel–Tammann–Fulcher (VTF) fitting parameters (T_0 , A and B).

No.	PEG mol. wt	Salt	PEGDME (wt%)	EO/M^+	ΔE_a (eV)	T_0 (K)	A (S cm^{-1})	B (eV)
1	4000	NaClO_4	–	30	0.66	286.7	0.035	0.014
				20	0.67	281.3	0.034	0.020
				15	0.64	298.7	0.044	0.019
				10	0.54	281	0.086	0.017
2	4000	NaBF_4	–	30	0.65	284.2	0.041	0.056
				20	0.69	300.3	0.043	0.053
				15	0.74	299.7	0.014	0.066
				10	0.63	281.9	0.053	0.064
3	4000	KI	–	30	0.70	211.1	0.144	0.080
				20	0.73	208.6	0.178	0.085
				15	0.81	246.9	0.167	0.045
				10	0.59	180.5	0.0227	0.076
4 ^b	4000	LiCF_3SO_3	–	20	0.52	181.4	0.0423	0.079
				15	0.57	186.3	0.0955	0.094
				10	0.52	187.5	0.1435	0.101
				30	0.58	188.6	0.0070	0.066
5 ^a	4000	LiClO_4	–	20	0.55	187.7	0.0049	0.055
				15	0.53	190.9	0.0013	0.027
				10	0.52	195.2	0.0008	0.015
				30	0.54	244.4	0.016	0.024
6	400	LiClO_4	–	20	0.80	179.2	0.086	0.097
				15	0.78	220.2	0.032	0.050
				10	0.78	251.1	0.048	0.043
				30	0.68	263.1	0.047	0.023
7	2000	LiClO_4	–	20	0.55	195.4	0.119	0.085
				15	0.70	245.9	0.091	0.037
				10	0.78	256.5	0.093	0.031
				30	0.59	248.7	0.031	0.027
8	10,000	LiClO_4	–	20	0.43	216.1	0.042	0.045
				15	0.45	274.4	0.017	0.014
				10	0.47	216.8	0.066	0.061
				30	0.52	262.9	0.020	0.019
9	35,000	LiClO_4	–	20	0.54	207.2	0.076	0.066
				15	0.59	187.8	0.116	0.092
				10	0.64	237.3	0.038	0.041
				30	–	166.6	0.874	0.116
10	4000	LiClO_4	10	15	–	229.1	0.203	0.042
				10	–	184.6	0.816	0.102
				20	–	259.2	0.111	0.017
				15	–	247.9	0.153	0.022
11	4000	LiClO_4	20	10	–	242.1	0.210	0.025
				20	–	238.6	0.428	0.040
				15	–	234.9	0.303	0.033
				10	–	252.9	0.216	0.021

^a Data from Ref. [40].

^b Data from Ref. [41].

a Teflon mould. The curing is initially done at room temperature for 24 h and subsequently at 80 °C for further 24 h to get the semi-IPN films of PEO–PU/PAN (60/40) doped with various salts. The salts used in the present study are NaClO₄, NaBF₄, KI along with LiClO₄ and LiCF₃SO₃.

2.2.2. Variation of PEG molecular weight

The LiClO₄ doped semi-IPNs with poly(ethylene glycol) of various molecular weight was achieved by adopting the similar synthetic strategy as described above. For the synthesis of the poly(ethylene oxide)–polyurethane networks the –OH/–NCO ratio was always maintained at 1:1.25. Poly(ethylene glycol) (PEG) of molecular weights 400, 2000, 4000, 10,000 and 35,000 were used in this study. The curing conditions remain the same as described in the previous section.

2.2.3. Oligomeric plasticization of the LiClO₄ doped semi-IPNs

Plasticization of the LiClO₄ doped semi-IPNs was achieved by the addition of polyethylene glycol dimethylether (PEGDME) to form a ternary semi-IPN system. The desired amount of plasticizer was mixed with PEG and dissolved in THF prior to its addition to the prepolymer along with the other components. Semi-IPNs incorporated with 10, 20 and 30 wt% plasticizer were thus synthesized. The curing conditions remain the same as described in the previous section.

2.3. Basic characterizations

The synthesis steps involved in the formation of the prepolymer, parent network and semi-IPN was followed with Fourier transform infra-red vibrational spectroscopy studies (see [Supporting information](#)). The FTIR spectra were recorded at room temperature in the range of 4000 to 400 cm^{−1} using a Bruker ALPHA-T Spectrometer after 256 scans with a wavenumber resolution of 4 cm^{−1}. The thermal properties were investigated on a Differential Scanning Analyzer 2010 (TA Instruments) and the DSC thermograms were recorded in the range of −120 to 150 °C with a scan rate of 10 °C min^{−1}.

2.3.1. Conductivity studies

The DC characteristics of the synthesized semi-IPN salt complexes of different compositions were studied on a Keithley 236 Source Measure Unit interfaced with an indigenously developed sample holder. The synthesized polymer electrolyte samples were vacuum dried overnight before carrying out the electrical measurements. The disc shaped polymer films (thickness ~ 0.6 mm) were sandwiched between two spring loaded platinum blocking electrodes each of surface area 0.8 cm² and a Teflon spacer ensured the application of same amount of spring pressure during the tests. The sample holder was placed in a thermostat controlled heating chamber in an inert atmosphere and shielded from external electrical disturbance to carry out variable temperature measurements in the range of 30–80 °C at an interval of 5 °C. The temperature was measured with accuracy better than ±0.2 °C using a platinum–rhodium thermocouple placed in close proximity with the sample. No corrections for thermal expansion of the cell were carried out. Resistance at each temperature was estimated from the reciprocal of slope obtained from the *I*–*V* curve. Analysis of the temperature dependence of the DC conductivity data was done by non-linear least square fits (NLSF) using Microcal Origin 6.0 software. The maximum error associated with the simulated fits for the Arrhenius and Vogel–Tammann–Fulcher (VTF) equation is within ±5%.

The electrochemical stability window of the electrolyte matrix was determined using linear sweep voltammetry in a Swagelok

three-electrode T-assembly, where a 316 stainless steel disk was used as the working electrode while lithium metal served as the counter electrode and reference. The spring load in the Swagelok assembly was ensured to apply similar pressure using Teflon spacer of appropriate dimensions. An anodic scan was carried out on the samples between 2.5 and 7 V at a scan rate of 10 mV s^{−1} and room temperature (30 °C) using a Zahner Zennium® electrochemical workstation.

3. Results and discussion

The study was initiated with the idea to rationalize (a) the effect of ion-dissociation and complexation of various salts, (b) the macromonomer chain length (PEG) in the PEO–PU network component and (c) the effect of oligomeric entanglements and plasticization by PEGDME on the ion conductivity in PEO–PU/PAN semi-IPN systems. During the course of our preliminary study on PEO–PU/PAN semi-IPNs doped with LiClO₄ and LiCF₃SO₃ it was observed that the concentration of the salt plays a significant role in shaping the morphology as well as increasing the conductivity of these systems [40–43]. It was evident from the results obtained from DSC studies that increasing the salt concentration restrict the growth of crystalline domains [40,41]. This was attributed to the formation of increased number of pseudo-crosslinks by the Li⁺ ions with the ether group (–C–O–C–, $\nu_s \sim 1110$ cm^{−1}) of the poly(ethylene oxide) segments in the semi-IPNs. Further, the IR-studies on LiCF₃SO₃ doped semi-IPNs also suggested the preferential dissolution of salt in the polyether phase making it progressively more amorphous [41]. It is understood that the nature of the salt, *i.e.* the cation/anion size and their charge density would also affect the ion–dipole interaction with the coordinating site of the polymer. This in turn influences the ionic mobility as well as the segmental flexibility of the polymer thus affecting the formation of crystalline domains, intermolecular transient crosslinks, and matrix phase composition which is also reflected in the magnitude of ionic conductivity.

3.1. Effect of salt

Fig. 1(a) shows the effect of various salts such as LiClO₄, LiCF₃SO₃, NaClO₄, NaBF₄ and KI on the DC conductivity of the semi-IPNs at 35 °C (~room temperature) as a function of the solvated salt concentration. With increase in salt concentration (decreasing EO/M⁺ ratio), the ionic conductivity increases steadily and beyond a critical electrolyte concentration (EO/M⁺ ratio different for each salt) it shows a rather rapid decrease. The increase in the number of charge carriers with salt concentration results in an increase in the conductivity. However, at higher salt contents, even though the carrier concentration increases, the alkali metal ions act as transient crosslinkers, resulting in progressive immobilization of the polymer chain segments, which thereby decreases the conductivity. The inference relating to increased formation of transient crosslinks within the system can be rationalized better when the effect of electrolyte concentration on glass transition temperature (*T*_g) is considered. Fig. 1(b) demonstrates the steady increase in *T*_g for decreasing EO/M⁺ ratio (*i.e.* increase in salt loading) typically for two systems, LiClO₄ and LiCF₃SO₃, respectively, strongly supports this contention.

Further, as observed from Fig. 1(a), the maximum conductivity was obtained for LiClO₄ doped semi-IPNs at an EO/Li ratio of ~ 10. The general trend that could be undoubtedly discerned for the maximum conductivity achieved among the various salts is: LiClO₄ ≥ LiCF₃SO₃ > NaBF₄ > NaClO₄ > KI; which can be explained on the following lines. In general, the formation of polymer electrolytes is controlled by the cation solvation energy. Smaller cations, which are highly electronegative with low polarizability

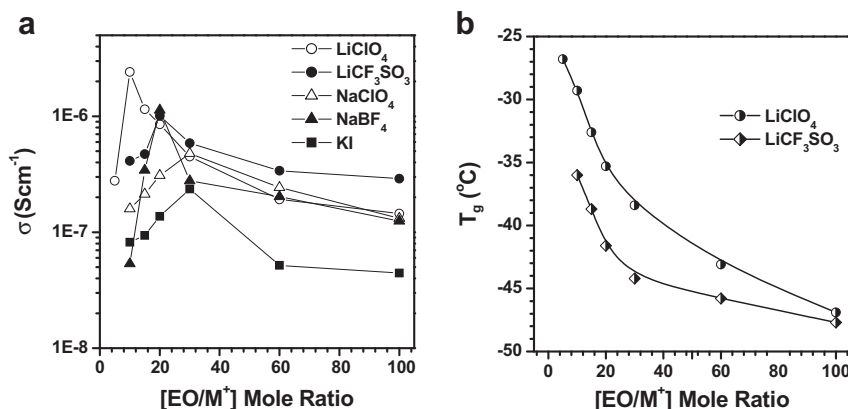


Fig. 1. Plots of (a) conductivity of PEO–PU/PAN semi-IPN electrolytes for different salts at 35 $^\circ\text{C}$ as a function of $[\text{EO}/\text{M}^+]$ mole ratio; (b) variation of glass transition temperature (T_g) with salt concentration for two typical systems LiClO_4 and LiCF_3SO_3 . Data on LiClO_4 and LiCF_3SO_3 systems are taken from Refs. [40,41].

tend to behave as hard acids and thus have better interaction with the ether oxygen (hard base) [11,19]. It is thus understandable that highly solvated ions such as Li^+ form better transient complexes (enhanced ion-dissociation) compared to that of Na^+ and K^+ . Thus, the lithium salts doped semi-IPNs show higher conductivity owing to better dissociation and free ion formation of the electrolytes in the matrix. The other parameter is the nature of anions, which also plays an equally important role in the conductivity behavior, as ionic conductivity is the result of migration of cations and anions in opposite directions. In an aprotic medium, anions with lower charge density and basicity get destabilized more easily. Large anions with delocalized charge are weak bases and possess low ion–dipole stabilization energies. In addition, their lattice energies are relatively low. Hence, for polymer electrolytes, the order of preference for anions can be represented as [11]: $\text{AsF}_6^- \sim \text{BF}_4^- > \text{CF}_3\text{SO}_3^- \sim \text{ClO}_4^- > \text{SCN}^- \sim \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$. In the present study, comparable conductivities were indeed observed for LiClO_4 and LiCF_3SO_3 doped semi-IPNs owing to similar lattice energy of perchlorate and triflate salts. Similarly NaBF_4 doped semi-IPNs showed higher conductivity compared to that of NaClO_4 doped semi-IPNs. The relatively larger tetrafluoroborate anion screens the Na^+ ions poorly thereby allowing facile interaction with the ether oxygen. This in turn aids better dissolution of NaBF_4 salt in the PEO–PU/PAN semi-IPNs resulting in higher conductivities.

The temperature dependence of ionic conductivity provides useful insights in the mechanism of ion transport and associated activation energy for ion hopping [40,41]. Fig. 2a–d shows the representative best fits for EO/M^+ ratios corresponding to the best composition for different salts. These observations can be explained considering the physical properties of such systems. In general, the typical temperature dependence of ionic conductivity in most systems usually increases linearly with increasing temperature, which can be to a first approximation well represented by the classical Arrhenius theory given by:

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \quad (1)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann constant. Most PEO based polymer–salt complexes are however, multiphase systems with both crystalline and amorphous regions. Ionic conduction in the polymer matrix is favored essentially in the amorphous domains of such systems. Polymer electrolytes with predominantly amorphous phase ion hopping can strongly couple with polymer segmental modes above the glass transition temperature. Hence, in amorphous polymer electrolytes, which are widely disorganized, the temperature

dependence of σ does not follow the simple Arrhenius behavior, but is found to obey the empirical Vogel–Tammann–Fulcher (VTF) equation which is non-linear [11].

$$\sigma = AT^{-1/2} \exp[-B/(T - T_0)] \quad (2)$$

where A , B and T_0 are the fitting parameters. ‘ A ’ is a constant that depends on the material property, ‘ B ’ is the pseudo-activation energy related to the segmental motion of the polymer chains and ‘ T_0 ’ is the equilibrium glass transition temperature or the ideal vitreous transition temperature. This T_0 is usually found to be 30–50 $^\circ\text{C}$ below T_g , where the configurational entropy of the system is assumed to be zero.

Close assessment of the data of $\log \sigma$ versus $1000/T$ plots (particularly in the EO/M^+ ratio of 30 to 10 for most salts used), the conductivity behavior of the semi-IPNs, showed a change from linear to non-linear domain at slightly elevated temperatures, which resembles VTF like behavior. The data was hence analyzed using both the Arrhenius and VTF equation fits. Interestingly, in the lower temperature region, up to ~ 328 K, the Arrhenius equation fits well and above this the VTF fit is found to be suitable. This strongly indicates the melting of reminiscent crystalline domains of PEG (crystalline melting temperature, T_m) in the PEG–PU network, softening the matrix, which in turn enhance the segmental mobility of the polymer chains facilitating ion conduction. This added participation of substantially higher segmental mobility within the matrix in addition to the conventional ionic hopping mechanism manifests itself as non-linear dependence on temperature. The fitting parameters for VTF and the resulting activation energies of both the Arrhenius and VTF fits obtained for semi-IPNs doped with NaClO_4 , NaBF_4 and KI are presented in Table 1. The temperature dependent behavior of conductivity for LiClO_4 , LiCF_3SO_3 , NaClO_4 , NaBF_4 and KI are provided in the supplementary information document.

3.2. Effect of poly(ethylene glycol) chain length

Ionic mobility in polymer electrolyte matrices is strongly dependent on the segmental motions of the polymer host. In network polymers, these internal-Brownian motions (segmental mobility) can be tuned by either varying the crosslink density or by varying the polymer chain length between the crosslinks. The DC conductivity profiles at 35 $^\circ\text{C}$ (room temperature) for the LiClO_4 loaded semi-IPNs containing poly(ethylene oxide) segments of various chain lengths are presented in Fig. 3. As can be observed from the plot, increase in the salt content (decrease in EO/Li^+ mole

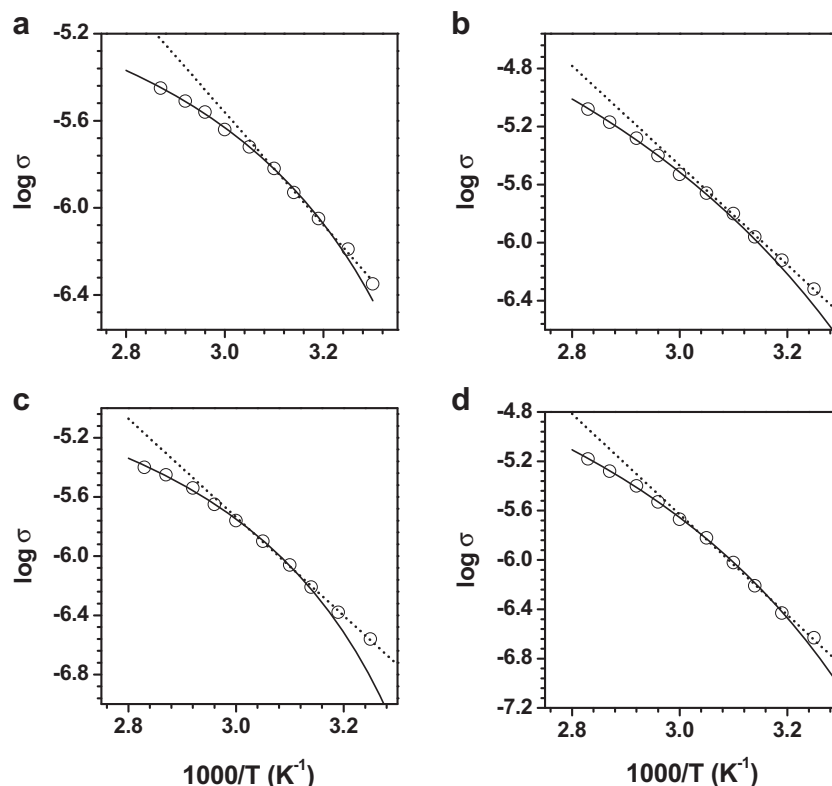


Fig. 2. Typical $\log \sigma$ versus $1000/T$ plots for PEO–PU/PAN 60/40 semi-IPN electrolytes with solvated salts (a) LiClO_4 (data from Ref. [40]), (b) NaClO_4 , (c) NaBF_4 and (d) KI at $[\text{EO}/\text{M}^+] = 30$. An Arrhenius-VTF transition at $\sim T_m = 50^\circ\text{C}$ (melting temperature) of the PEG crystalline domains is observed in the temperature dependence of conductivity behavior for all the compositions depicted. The dashed and solid lines in the plots are the fits to Arrhenius equation and VTF model, respectively.

ratio) for all the compositions leads to an initial steady rise in ionic conductivity, due to the increase in the number of charge carriers. Nevertheless, the conductivity decreases after a critical salt concentration, which could be undoubtedly attributed to the restricted segmental mobility of the polymer chains due to the formation of larger number of Li^+ ion mediated pseudo-crosslinks as supported by our DSC studies discussed in the preceding section.

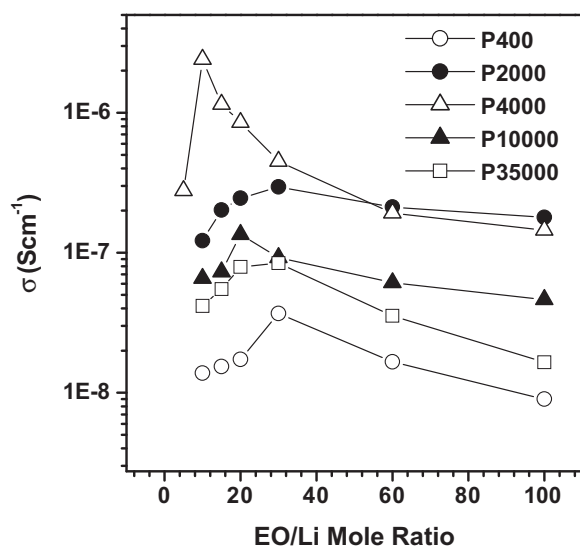


Fig. 3. Comparative variation of conductivity (σ) at 35°C as a function of EO/Li ratio for PEO–PU/PAN semi-IPN 60/40 electrolytes with LiClO_4 as the solvated salt synthesized using different molecular weight PEG in the PEO–PU matrix. Data on P4000 system from Ref. [40].

An additional interesting observation that can be made from the plot is the influence of the PEG chain length on the conductivity. The study was initiated with the idea to improve on the conductivity levels of the PEO–PU/PAN semi-IPN systems obtained using an arbitrary molecular weight of PEG-4000. Varying the chain length of PEG during synthesis provides a simple alternative of tailoring the system. However, contrary to our expectations the variation in the chain length was found to adversely affect the conductivity of the semi-IPNs already achieved using PEG-4000, which can be explained along the following lines. The shortening of the chain length using same amounts of PEG-2000 and PEG-400 during synthesis while maintaining the $-\text{OH}/-\text{NCO}$ ratio of 1:1.25, leads to a phenomenal increase in the number of chemical crosslinks in the system. This in turn severely restricts the mobility of chain segments between two crosslinks that manifests as a marked decrease in the overall conductivity.

Alternatively, the degree of crosslinking can be lowered using higher molecular weight PEG (10,000 and 35,000) in the semi-IPNs. Nevertheless, the attempt toward increasing the chain length was also found unfavorable for ion conductivity. The progressive decrease in the conductivity with increase in the molecular weight of the PEG can be attributed to the propensity to form crystalline domains which is a favored morphology of higher molecular weight PEGs. It is now well understood for salt-in-polymer systems, that ionic conductivity is impaired in the highly H-bonded crystalline regions of the polymer electrolytes due to the slower segmental motions. As a consequence, the DC conductivity in the PEG-10,000 and PEG-35,000 semi-IPNs was found to be significantly low. Thus, it can be inferred, that in these network polymer electrolytes of PEO–PU/PAN semi-IPNs, an optimal polymer chain length between the crosslinks is necessary to have a better ion-conductivity response. In the present comparative

study, the randomly chosen PEO–PU/PAN semi-IPN system with PEG-4000, was found to effectively satisfy this criteria.

The temperature dependence of ionic conductivity for the semi-IPNs with various PEG chain length are presented in Fig. 4a–d. As also observed in earlier cases, the conductivity behavior of the semi-IPNs showed an Arrhenius to VTF transition around ~ 323 K. However, in the case of semi-IPNs synthesized from PEG-10,000 and PEG-35,000 these deviations from Arrhenius to VTF behavior are not very prominent. This could largely be attributed to the high degree of crystallinity in these systems associated with the high molecular weight PEG used. It is probable that a considerable amount of crystalline domains exists in these systems within the temperature window studied. A similar observation was noted in the case of PEG-4000 semi-IPNs of EO/Li⁺ composition 100 and 60, wherein DSC results indicated the presence of considerable amount of crystallinity [40]. The fitting parameters for VTF and the resulting activation energies of both the Arrhenius and VTF fits obtained for various semi-IPNs are summed up in Table 1.

3.3. Effect of oligomeric plasticization

One popular approach to enhance segmental mobility in such network systems is the plasticization of the polymer matrix. Thus, it is pertinent to evaluate the effect of plasticization on the structural conformation and the ion-conductivity behavior of PEO–PU/PAN semi-IPNs. Low molecular weight diluent or ‘plasticizer’ has been widely used to enhance the properties of polymer electrolytes for a number of applications [22–25]. The polymer matrix acts as a host for these highly viscous liquids, which interpenetrates or swells the polymer. Ideally the plasticized system would provide liquid-like ionic conductivity, while preserving the dimensional stability of such *gel*-polymer electrolytes. It has been often observed that the polymer electrolytes with low molecular weight plasticizers such as ethylene carbonate (EC) and propylene

carbonate (PC) show a marked increase in their conductivity by two to three orders of magnitude. Nevertheless, the problem associated with solvent loss leaves the electrolytes not only with indeterminate composition but also deteriorates its ionic conductivity with time leading to poor performance and life-time issues for practical devices [26,27]. To minimize the solvent evaporation, low molecular weight poly(ethylene glycols) have been used quite often as plasticizers as their low viscosity facilitates ion diffusion [28–34]. However, low molecular weight PEGs with hydroxyl end groups were found to be very reactive to lithium electrodes and forms a considerably high-impedance solid electrolyte interface (SEI) between the lithium electrode and the electrolyte, thus, adversely affecting the performance of the cell [45]. On these grounds, we have chosen a low molecular weight, nonvolatile, methoxy terminated nonreactive poly(ethylene glycol) dimethylether (PEGDME 500) as the oligomeric plasticizer for the present study.

From our earlier studies, PEO–PU/PAN (60/40) semi-IPNs synthesized using PEG-4000 with LiClO₄ as the electrolyte has yielded the highest conductivity levels. Hence, we have proceeded with this particular system to create a ternary system using PEGDME (MW = 500) and study the effect of additional oligomeric entanglements. Fig. 5(a) shows DC conductivity as a function of EO/Li ratio for semi-IPNs with different amount of PEGDME content in the matrix at 35 °C. That the ternary system so synthesized facilitates the process of ion transport is quite evident from the noticeable increase in the conductivity assessment. As can be observed, the ionic conductivity increases steadily with increase in the amount of plasticization of the matrix and showed an increase of one order of magnitude from $\sim 2.4 \times 10^{-6} \text{ S cm}^{-1}$ to $\sim 2 \times 10^{-5} \text{ S cm}^{-1}$. Even so, the effect of incorporated oligomer on the conductivity is more pronounced with increase in temperature. Significantly, the ionic conductivity at 80 °C was approximately found to be two orders higher ($\sim 2 \times 10^{-4} \text{ S cm}^{-1}$) when compared to that of un-plasticized semi-IPNs ($\sim 6 \times 10^{-6} \text{ S cm}^{-1}$) (Fig. 5(b)).

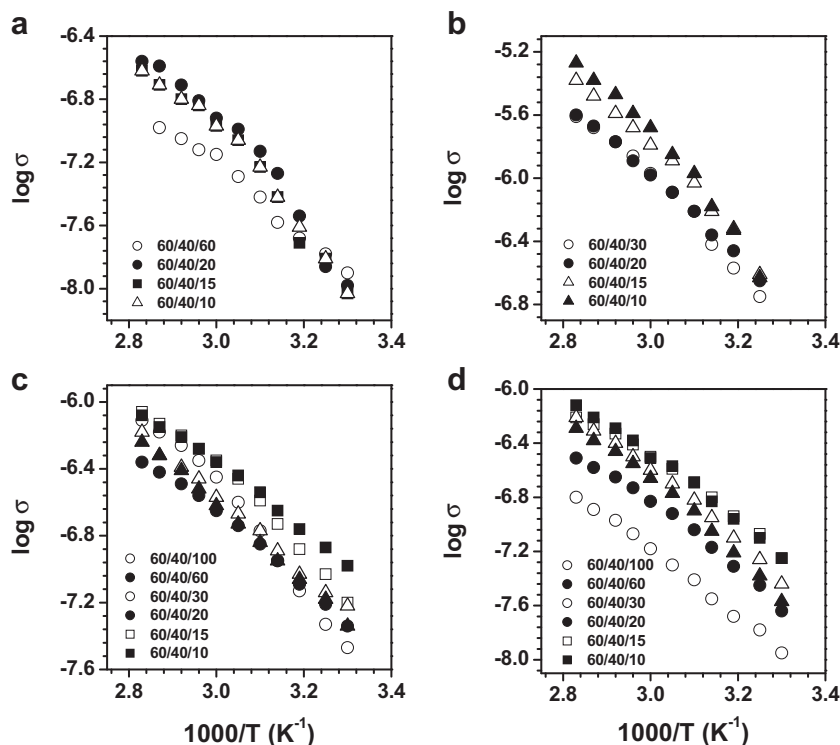


Fig. 4. Typical $\log \sigma$ versus $1000/T$ plots for PEO–PU/PAN semi-IPN 60/40 synthesized using (a) PEG-400, (b) PEG-2000, (c) PEG-10,000, and (d) PEG-35,000 for various salt concentration.

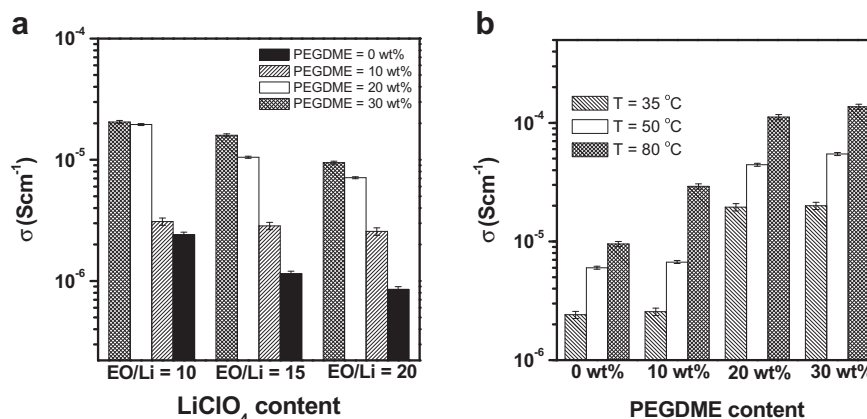


Fig. 5. Plots of (a) variation of conductivity (σ) at 35 °C with EO/Li ratio for PEO–PU/PAN semi-IPN 60/40 with LiClO_4 for different weight percent of oligomeric plasticization (PEGDME); (b) variation of conductivity as a function of PEGDME content at different temperatures.

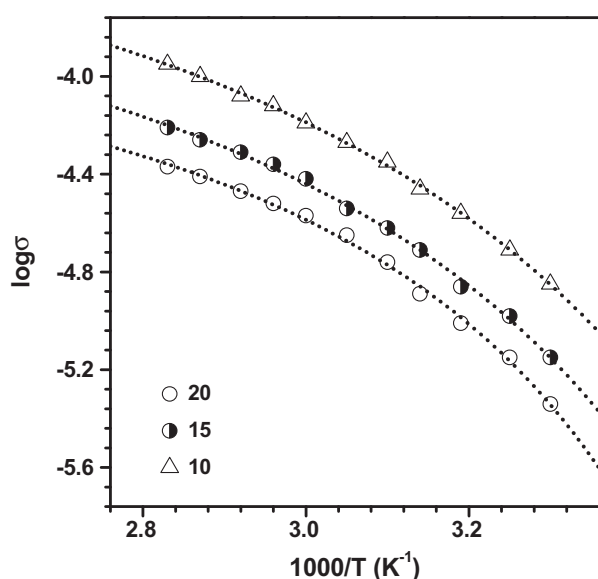


Fig. 6. Typical $\log \sigma$ versus $1000/T$ plots for PEO–PU/PAN/ LiClO_4 semi-IPN electrolytes (60/40) with 20 wt% PEGDME content at three different EO/Li mole ratio. The dashed line represents the fit to VTF model throughout the temperature window under study.

The use of PEGDME as an oligomeric plasticizer not only enhances the solvation of the salt but also enhances the segmental mobility in the semi-IPN matrix while retaining the film formability of the system. This was further substantiated from the $\log \sigma$ versus $1000/T$ plots for the ternary semi-IPNs of different PEGDME and EO/Li compositions as presented in Fig. 6 and Supporting information. It was observed that the VTF behavior is followed throughout the temperature window studied which implies a liquid-like environment for the ionic charge carriers. The oligomer PEGDME used interpenetrates uniformly well throughout the PEO–PU/PAN semi-IPN polymer matrix, and these entanglement zones provides a co-continuous channels within the network that enhances ion conduction. The fitting parameters for VTF equation for various semi-IPNs are provided in Table 1.

It is pertinent to determine the electrochemical stability window to evaluate the feasibility of these materials for potential application as electrolytes in lithium–ion batteries. Fig. 7 shows a typical current (I) versus voltage (E) linear sweep voltammetry response (anodic scan) obtained using SS 316 working electrode and Li-metal used as counter as well as reference for a salt and

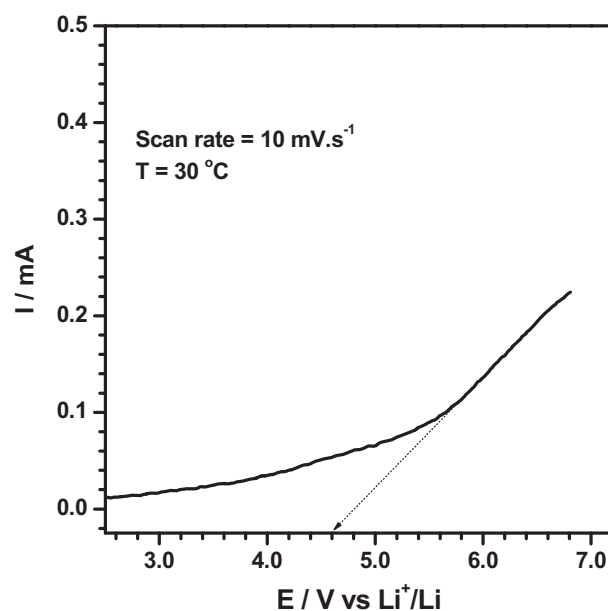


Fig. 7. Typical linear sweep voltammetry response (anodic scan) obtained for a salt and plasticizer optimized ternary system semi-IPN electrolyte matrix (PEO–PU/PAN 60/40, LiClO_4 , EO/Li^+ mole ratio = 10, PEGDME 500 = 30 wt%). A Swagelok three-electrode T-assembly with a 316 stainless steel disk was used as the working electrode while lithium metal served as the counter electrode and reference.

plasticizer optimized electrolyte matrix (PEO–PU/PAN 60/40, LiClO_4 , EO/Li^+ mole ratio = 10, PEGDME 500 = 30 wt%). As indicated in the figure, the onset of electrochemical decomposition of the electrolyte is found to be ~ 4.6 V where an irreversible anion oxidation occurs at SS 316 working electrode. The observation suggests that the systems are considerably stable and could be paired up with most of the popular cathode/anode materials operating within such voltage range.

4. Conclusions

To sum up, the effect of simple structural modifications using various salts, PEG chain length and oligomeric plasticization on the DC conductivity behavior of a promising system, PEO–PU/PAN semi-IPNs has been evaluated. The maximum conductivity for the semi-IPN composition 60/40 doped with different salts shows the trend: $\text{LiClO}_4 \geq \text{LiCF}_3\text{SO}_3 > \text{NaBF}_4 > \text{NaClO}_4 > \text{KI}$. The temperature

dependent conductivity behavior for all the compositions showed Arrhenius to VTF transition ~ 323 K. This change over could be attributed to the slow transformation of the semicrystalline domains in the polymer matrix to amorphous phase. The studies on crosslink density suggest that the PEG chain length or the molecular weight between the crosslinks is indeed a determining factor to achieve good conductivity levels. An optimal conductivity for PEO–PU/PAN semi-IPNs was achieved using a poly(ethylene glycol) molecular weight of 4000. The Arrhenius to VTF transition in these semi-IPNs demonstrate that the temperature dependence of conductivity follows a general trend which is mostly independent of the nature of salt and the poly(ethylene glycol) chain length used. Oligomeric plasticization of the semi-IPN matrix was achieved using poly(ethyleneglycol dimethylether). The conductivity of the PEO–PU/PAN/LiClO₄ semi-IPNs showed a steady increase with the extent of oligomeric entrapment. Semi-IPN composition containing 30 wt% PEGDME yielded ionic conductivity of $\sim 2 \times 10^{-5}$ S cm⁻¹ at 35 °C which is an order of magnitude higher than that obtained without plasticization. The VTF behavior throughout the temperature window studied for the ternary system suggests that entangled oligomers provide a liquid-like environment that assists in ionic conduction. Linear sweep voltammetry indicates significantly good electrochemical stability (~ 4.6 V) of the polymer electrolyte matrix. Overall, these results validate our original contention of using a semi-IPN system as SPE, which can be suitably custom designed using simple structural modifications.

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Appendix A. Supporting information available

The complete details of PEG–PU/PAN semi-IPN synthesis along with the individual FTIR spectrum obtained at different stages of prepolymer, network and semi-IPN formation along with the plots for temperature dependence of ionic conductivity for all the systems discussed in the manuscript. This material can be found, in the online, version at <http://dx.doi.org/10.1016/j.jpowsour.2012.05.075>.

References

- [1] Y. Ikeda, J. Appl. Polym. Sci. 78 (2000) 1530.
- [2] S. Kohjiya, Y. Ikeda, Mater. Sci. Res. Int. 4 (1998) 73.

- [3] S. Kohjiya, T. Kawabata, K. Maeda, S. Yamashita, Y. Shibata, in: B. Scrosati (Ed.), Second International Symposium on Polymer Electrolytes, Elsevier, London, 1990.
- [4] Y. Matoba, Y. Ikeda, S. Kohjiya, Solid State Ionics 147 (2002) 403.
- [5] Y. Ikeda, H. Masui, S. Shoji, T. Sakashita, Y. Matoba, S. Kohjiya, Polym. Int. 43 (1997) 269.
- [6] A. Nishimoto, M. Watanabe, Y. Ikeda, S. Kohjiya, Electrochim. Acta 43 (1998) 1177.
- [7] Y. Ikeda, Y. Wada, Y. Matoba, S. Murakami, S. Kohjiya, Rubber Chem. Technol. 73 (2000) 720.
- [8] Y. Ikeda, Y. Wada, Y. Matoba, S. Murakami, S. Kohjiya, Electrochim. Acta 45 (2000) 1167.
- [9] M. Watanabe, S. Oohashi, K. Sanui, N. Ogata, T. Kobayashi, Z. Ohataki, Macromolecules 18 (1985) 1945.
- [10] C. Robitaille, J. Prud'homme, Macromolecules 16 (1983) 665.
- [11] F.M. Gray (Ed.), Solid Polymer Electrolytes-Fundamentals and Technological Applications, VCH, Weinheim, Germany, 1991.
- [12] D.W. Xia, D. Soltz, J. Smid, Solid State Ionics 14 (1984) 221.
- [13] N. Kobayashi, M. Uchiyama, K. Shigehara, E. Tsuchida, J. Phys. Chem. 89 (1985) 987.
- [14] D.J. Banister, G.R. Davies, I.M. Ward, J.E. McIntyre, Polymer 25 (1984) 1600.
- [15] J.F. LeNest, H. Cheradame, F. Dalard, D. Derou, J. Appl. Electrochem. 16 (1986) 75.
- [16] A. Killis, J.F. LeNest, A. Gandini, H. Cheradame, J.P. Cohen-Addad, Solid State Ionics 14 (1984) 231.
- [17] A. Killis, J.F. LeNest, H. Cheradame, J.P. Cohen-Addad, Polym. Bull. 6 (1982) 351.
- [18] M. Andrei, M. Soprani, Polymer 39 (1998) 7041.
- [19] J.M.G. Cowie, S.H. Cree, Annu. Rev. Phys. Chem. 40 (1989) 85.
- [20] X. Andrieu, J.P. Boueve, T. Vicedo, J. Power Sources 43–44 (1993) 195.
- [21] M. Clericuzio, W.O. Parker Jr., M. Soprani, X. Andrieu, Solid State Ionics 82 (1995) 179.
- [22] M. Alamgir, K.M. Abraham, in: G. Pistoia (Ed.), Lithium Batteries-New Materials, Developments and Perspectives, Elsevier, Amsterdam, 1994.
- [23] M.H. Sheldon, M.D. Glasse, R.J. Latham, R.G. Linford, Solid State Ionics 34 (1989) 135.
- [24] G.B. Appeterechi, F. Groce, B. Scrosati, Electrochim. Acta 40 (1995) 991.
- [25] Z. Jiang, B. Carroll, K.M. Abraham, Electrochim. Acta 42 (1997) 2667.
- [26] M. Alamgir, R.D. Moulton, K.M. Abraham, in: K.M. Abraham, M. Salomon (Eds.), Primary and Secondary Lithium Batteries, Electrochem. Soc. Pennington, N.J., 1991.
- [27] F. Groce, F. Gerace, G. Dautzemberg, S. Passerini, G.B. Appeterechi, B. Scrosati, Electrochim. Acta 39 (1994) 2187.
- [28] I. Kelly, J.F. Owen, B.C.H. Steele, J. Electroanal. Chem. 168 (1984) 467.
- [29] Y. Ito, K. Kanehori, K. Miyauchi, T. Kudo, J. Mater. Sci. 22 (1987) 1845.
- [30] K.M. Abraham, M. Alamgir, R.K. Reynolds, J. Electrochem. Soc. 135 (1988) 535.
- [31] L. Yang, J. Lin, Z. Wang, C. Wang, R. Zhaou, Q. Liu, Solid State Ionics 40–41 (1990) 616.
- [32] K.M. Abraham, Z. Jiang, B. Carroll, Chem. Mater. 9 (1997) 1978.
- [33] K.M. Abraham, Z. Jiang, J. Electrochem. Soc. 144 (1997) 136.
- [34] Y. Kato, S. Yokoyama, H. Ikuta, Y. Uchimoto, M. Wakihara, Electrochem. Commun. 3 (2001) 128.
- [35] Y. Kato, K. Hasumi, S. Yokoyama, T. Yabe, H. Ikuta, Y. Uchimoto, M. Wakihara, Solid State Ionics 150 (2002) 355.
- [36] S.T.C. Ng, C. Jolliffe, A. Goodwin, M. Forsyth, D.R. MacFarlane, Electrochim. Acta 43 (1998) 1499.
- [37] Y. Ahira, M. Kodama, K. Nakahara, H. Okise, K. Murata, J. Power Sources 65 (1997) 143.
- [38] C.J. Leo, G.V.S. Rao, B.V.R. Chowdari, Solid State Ionics 148 (2002) 159.
- [39] Y.-T. Kim, E.S. Smotkin, Solid State Ionics 149 (2002) 29.
- [40] P. Basak, S.V. Manorama, Solid State Ionics 167 (2004) 113.
- [41] P. Basak, S.V. Manorama, Eur. Polym. J. 40 (2004) 1155.
- [42] P. Basak, S.V. Manorama, R.K. Singh, O. Parkash, J. Phys. Chem. B 109 (2005) 1174.
- [43] P. Basak, S.V. Manorama, J. Macromol. Sci. Pure Appl. Chem. A43 (2006) 369.
- [44] Md.S.A. Sher Shah, P. Basak, S.V. Manorama, J. Phys. Chem. C 114 (2010) 14281.
- [45] W. Preechatiwong, J.M. Schultz, Polymer 37 (1996) 5109.